

Improved steel composition

Patent number: EP1087029
Publication date: 2001-03-28
Inventor: FRYER JOHN EDWIN (GB); WARDALL STUART DAVID (GB)
Applicant: HEYMARK METALS LTD (GB)
Classification:
- **international:** C22C38/38
- **european:** C22C38/00B, C22C38/38, C22C38/44
Application number: EP20000107561 20000407
Priority number(s): GB19990022757 19990927

Also published as:

 GB2345491 (A)
 EP1087029 (A3)

Cited documents:

 DE4242757
 GB778597
 FR2493344
 JP10121203
 JP61238943

Abstract of EP1087029

The invention relates to a steel composition which is substantially free of nickel and which can be used for medical implants and/or jewellery manufacture. Some humans experience severe allergic reactions to Nickel and therefore there has been a desire for some time to provide a Nickel free steel. Nickel is an important constituent of surgical grade steel because it is a good austenite promoter, and steel thus formed has good strength properties and has paramagnetic characteristics which are essential for such steels. The absence of Nickel results in the formation of ferritic steel which is ferromagnetic, which cannot be used for medical implants. The invention results from the realisation that Nitrogen is a good promoter of austenitic steel structures, and although Nitrogen is a gas and thus generally insoluble in molten steel, a careful balance of additional alloying elements such as Manganese, Chromium, and Molybdenum, with Iron can result in a molten alloy in which Nitrogen can be dissolved at atmospheric pressure to a degree at which its austenitic steel structure promotion effects are readily appreciable.

Data supplied from the **esp@cenet** database - Worldwide



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 087 029 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.03.2001 Bulletin 2001/13(51) Int. Cl.⁷: C22C 38/38

(21) Application number: 00107561.3

(22) Date of filing: 07.04.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 27.09.1999 GB 9922757

(71) Applicant:
Heymark Metals Limited
Bar Lane Industrial Estate, Roeciff,
Boroughbridge YO51 9NR (GB)

(72) Inventors:
• Wardall, Stuart David,
c/o Heymark Metals Ltd.
Roeciff, Boroughbridge YO51 9NR (GB)
• Fryer, John Edwin,
c/o Heymark Metals Limited
Roeciff, Boroughbridge YO51 9NR (GB)

(74) Representative: Denmark, James
Bailey, Walsh & Co.
5 York Place
Leeds LS1 2SD Yorkshire (GB)

(54) Improved steel composition

(57) The invention relates to a steel composition which is substantially free of nickel and which can be used for medical implants and/or jewellery manufacture. Some humans experience severe allergic reactions to Nickel and therefore there has been a desire for some time to provide a Nickel free steel. Nickel is an important constituent of surgical grade steel because it is a good austenite promoter, and steel thus formed has good strength properties and has paramagnetic characteristics which are essential for such steels. The absence of Nickel results in the formation of ferritic steel which is ferromagnetic, which cannot be used for medical implants. The invention results from the realisation that Nitrogen is a good promoter of austenitic steel structures, and although Nitrogen is a gas and thus generally insoluble in molten steel, a careful balance of additional alloying elements such as Manganese, Chromium, and Molybdenum, with Iron can result in a molten alloy in which Nitrogen can be dissolved at atmospheric pressure to a degree at which its austenitic steel structure promotion effects are readily appreciable.

EP 1 087 029 A2

Description

- [0001] This invention relates to an improved austenitic stainless steel composition which is comparatively ductile, has good corrosion resistance, has adequate biocompatibility, is readily cold worked to produce a product with excellent strength and ductility, machineability and is non magnetic under all conditions and more particularly to a steel which contains essentially no nickel.
- [0002] The standard well known austenitic stainless steels, containing generally 16-20% of chromium, 8-15% of nickel and 2-4% of molybdenum, are used in a wide variety of applications where their properties of good corrosion resistance, high strength, ductility and non-magnetic properties are well known.
- [0003] Because of these properties, a number of these compositions of austenitic stainless steels have found applications relating to repair and ornamentation of the human body. In the case of steels for human medical implant devices a number of specific chemical compositions have been developed and approved by certification bodies, namely those containing sufficient chromium, nickel, and molybdenum so as to prevent significant corrosion, particularly by chloride containing media, over a prolonged period of time. In the case of steels for bodily ornamentation, such as jewellery, watches, buckles, buttons and zip fasteners etc, a slightly leaner chemical composition, i.e. a lower weight percentage of the more expensive constituent elements Nickel and Molybdenum, is often employed as the corrosion risk is somewhat reduced and failure of the component is not as critical.
- [0004] Over the last few years however, jewellery manufacturers have increasingly preferred to use the medical implant grades of stainless steel for the manufacture of ornaments used in body piercing as this was seen to be of commercial advantage on account of the perceived reduction in potential product liability claims which could be experienced by the manufacturer of jewellery. Additionally, there are perceived marketing advantages in manufacturing jewellery from medical implant grade steel.
- [0005] Whilst all the steel compositions described above provide an ideal combination of properties for these applications, medical researchers and practitioners have long known that the metal nickel (and other metals to a lesser extent) can react with sweat and produce metal ions which can cause a severe allergic reaction in some people. It has also been shown that regardless of how the nickel is present in a metal, i.e. a mixture, a solid solution or in the form of metallic phases, the dose of metal ions required to cause an allergic reaction is dependent on the ease of release of the ion and not on the concentration of the ion present in the metal.
- [0006] In stainless steels for surgical implantation, nickel is an essential alloying element and it has become necessary to test patients for nickel allergy prior to an operation. Those patients found to give a positive response to the test must then have an implant made from nickel free materials which traditionally have inferior properties to the austenitic grades, limiting the choice to the significantly more expensive titanium and cobalt alloys.
- [0007] For the jewellery manufacturer or a retailer selling direct to the public, such a test would be wholly impractical. Consequently, a Council Directive (76/769) from the European Union has been implemented which "prohibits the use of cosmetic products which are liable to cause damage to human health" and in particular relevance to this patent specification "Nickel may not be used: in post assemblies which are inserted in to pierced ears or other pierced parts of the human body..... unless such post assemblies are homogeneous and the concentration of nickel expressed as mass of nickel to total mass is less than 0.05%". In addition, the directive also states that the nickel release rate of other products which contact the skin shall not exceed $0.5 \mu\text{g}/\text{cm}^2/\text{week}$.
- [0008] The result of this directive is to prohibit the use of all conventional austenitic stainless steels because an essential ingredient in their composition is nickel. This severely limits the choice of materials for jewellery from the expensive materials gold, silver, platinum, titanium etc. or inadequate (by virtue of their poor corrosion resistance, low strengths, and being ferromagnetic) ferritic or equally undesirable brittle martensitic stainless steels.
- [0009] Austenitic stainless steels represent the largest group of stainless steels in use. The term "Austenitic" refers to the atomic structure of the alloy at room temperature which in this case is arranged in the form of a face centred cube (FCC). In iron, low carbon steels and ferritic stainless steels, the atomic arrangement is somewhat different being in the form of a body centred cube (BCC). When heated the BCC steels transform to an FCC structure at a temperature of approximately 750 to 800°C together with a change in magnetic properties from being ferromagnetic (can be attracted by a magnet) to being paramagnetic (nonmagnetic). When the hot steel is now cooled this change is reversed and the steel once again becomes ferromagnetic with a BCC structure.
- [0010] By the addition of typically 8% nickel to ferritic stainless steels of approximately 18% chromium this transition to a BCC structure is suppressed to a temperature below room temperature and the nonmagnetic austenitic FCC structure is preserved. Thus, traditional austenitic stainless steels are those that use nickel to stabilise the FCC structure at several temperatures with all the aforementioned property advantages.
- [0011] The prohibition of the use of nickel as an alloying element and the tendency of the industry to adopt austenitic stainless steel alloys has forced steel manufacturers to explore alternative steel compositions incorporating other elements known to be favourable for the promotion of an austenitic structure. It has been found that of these other elements the most significant are carbon, nitrogen, manganese, cobalt and copper.

[0012] It is therefore a primary object of this invention to provide a substantially nickel free steel which is not prohibitively expensive for use as raw material for high volume jewellery manufacture or for medical implants, and which furthermore possesses some of the characteristics of currently available nickel steels.

5 [0013] It is a further the object of the invention to provide a stainless steel which is fully austenitic but which does not contain as an essential alloying element any nickel and does not contain any nickel as a residual at levels above 0.050% by weight and moreover does not release nickel ions in the present of bodily fluids so that an allergic reaction with human tissue is prevented.

10 [0014] Another object of the invention is to provide such an austenitic stainless steel which readily lends itself to hot working and cold working into a wide variety of products such as bars, rods, wires, plates and strip, which can be further fabricated to products of ultimate use by such processes as bending, coiling, cold drawing, machining, threading, cutting, polishing and the like.

15 [0015] A further object is to provide a stainless steel which is fully austenitic at room and cryogenic temperatures, is substantially free from ferrite, is paramagnetic, exhibits good corrosion resistance particularly in respect of chlorides, and can be provided in a wide variety of strength levels in excess of the standard austenitic stainless steels but retaining good ductility.

20 [0016] The present invention provides an austenitic stainless steel having as essential alloying elements: 0 to 0.15% of carbon, 0 to 0.3% of silicon, 12 to 25% of manganese, 12 to 20% of chromium, 0 to 2.4% of molybdenum, 0.3 to 0.55% of nitrogen, and from 0 to 10% of cobalt, 0 to 0.9% of copper, all percentages being percentages by weight, the remainder being iron together with incidental impurities and a concentration of nickel or less than 0.050%.

25 [0017] Particular preferred austenitic stainless steels in accordance with this invention are those in which the contents of alloying elements are: carbon 0 to 0.09%, silicon 0 to 0.3%, manganese 14 to 15%, chromium 16 to 18%, molybdenum 2.0 to 2.4%, nitrogen 0.45 to 0.55%, nickel 0.048% maximum.

[0018] Preferably the steel composition has amounts of Mn at 15% and Cr at 17%.

[0019] The most preferred composition is

25	C	0.09%
	Mn	17%
	Cr	15%
	N	0.45%
30	Mo	2.2%
	Ni	0.04%
	Fe	65.22%.

35 [0020] In certain circumstances austenite stabilisation may be aided by the addition of cobalt up to a maximum of 10% plus a small copper addition up to 0.9%.

[0021] It should be noted that other elements, for example silicon for deoxidation, may be desirable in small quantities and traces of other elements present as impurities may be contained in the new steel without detriment.

40 [0022] The elements cobalt and copper will usually be present in incidental amounts which are not detrimental. Their concentration may be increased from the incidental level to a higher level to improve the properties of the steels of the invention.

45 [0023] We have thus surprisingly found that all the nickel previously required to maintain the austenitic structure of the steel can, by a careful balance of these other elements, be totally replaced. The resulting alloy reproduces all the desirable properties of the nickel containing steel in terms of austenite stability, corrosion resistance, and paramagnetic characteristics and outperforms available Nickel steels in terms of strength and ductility and yet can still be fabricated and machined.

[0024] A more complete understanding of the invention is now provided by way of example with reference to the following Figures wherein:

Figure 1 shows a graph of the effect of Nickel and Chromium equivalents on the structure of stainless steel;

50 Figure 2 shows a bar chart of the resistance of various steel types to corrosion in the presence of differing acids at 1% concentration and at 80°C;

55 Figure 3 shows a graph of the Anodic polarisation curves for 316 and 17-15 Cr-Mn stainless steels in 0.6M Sodium Chloride, and

Figure 4 shows a graph of the work hardening and ductility characteristics of both Nickel-free and 302 Type steels.

[0025] Hereinafter, the designation "17-15" is applied to examples of the steels of this invention from cast numbers 11537 and 11985 and the steels designated 302-type, 316-type are austenitic stainless steels in accordance with British Standard BS 970 part 3 1991 and the steel designated composition "D" is in accordance with British Standard 7252 part 1 1997. All the various steels discussed herein will be well known to persons skilled in the art.

5 [0026] An essential starting point for the design of the alloy was that it should contain 16 to 18% of chromium as this is the element which provides the majority of the corrosion resistance of all stainless steels and at this level a generally acceptable degree of corrosion protection can be expected.

10 [0027] In Figure 1 the relationship between chromium/chromium equivalent elements (ferrite or BCC forming tendency) and nickel/nickel equivalent elements (austenite or FCC forming tendency) is demonstrated. It can be seen that for chromium levels of the order 18% a minimum equivalent of 12% of nickel or nickel equivalent elements would be required to provide a fully austenitic stainless steel.

15 [0028] To further enhance corrosion resistance and provide a steel with a similar level of corrosion resisting elements to those currently in use for medical and cosmetic applications, a minimum level of the rust resisting element molybdenum was considered essential. One drawback of the addition of molybdenum is that, like chromium, this element also has ferrite forming properties. In combination chromium and molybdenum represent a chromium equivalent of 20% which requires a nickel equivalent of 14% to maintain a fully austenitic structure.

20 [0029] As it was a prerequisite that nickel content had to be maintained at a level of <0.050% it was necessary to discover a combination of other nickel equivalent or austenite forming elements that could be used as a replacement.

25 [0030] Disregarding a number of expensive, rare and sometimes harmful elements such as platinum, palladium, rhodium and others, all of which are known to have austenite forming properties, it was established that manganese, nitrogen, carbon, cobalt and copper were probably the most favourable nickel replacing additions.

30 [0031] In deciding the final mixture of elements a number of interrelated metallurgical factors had to be taken into account. A high manganese content is desirable as it exhibits good austenite forming properties and is a relatively cheap and a readily available element. Too much manganese however can promote the formation of ferrite at hot working temperatures which may be retained after rapid cooling to room temperature. This would be undesirable as the alloy would exhibit some ferromagnetic tendencies. Carbon is a very strong austenite stabiliser but above approximately 0.15% it is very difficult to prevent the formation of undesirable chromium carbides which can render the steel brittle and can reduce corrosion resistance by precipitation at the steel grain boundaries. Nitrogen, like carbon is also a very potent austenite stabiliser; unfortunately, being a gas, the element has little solubility in steel especially during melting at temperatures of typically 1500 - 1600°C. In recent years researchers have developed metal re-melting techniques which can be performed at pressures well above atmospheric pressure and under these conditions high concentrations of nitrogen can be introduced. However, this equipment is expensive and unwieldy as it must produce significant positive pressure differentials above the furnace, and it was considered preferential to provide an alloy which could be manufactured using conventional and readily available furnaces. Consequently by careful adjustment of chromium manganese and molybdenum (all of which promote solubility of nitrogen) a composition was derived which would allow nitrogen solubility of typically 0.55% at normal atmospheric pressures. The careful adjustment has resulted in the claimed steel composition, and it is only within the ranges provided in the claim that Nitrogen can be forced to dissolve in the molten alloy to such a degree which prevents the formation of ferritic steel components at room temperature.

35 [0032] This level of nitrogen is also beneficial in terms of corrosion resistance as it has been shown that when present in combination with molybdenum a significant improvement in corrosion resistance can result.

40 [0033] Consideration was given to austenite stability at sub-zero or cryogenic temperatures and also stability after cold deformation. When austenitic stainless steels are subject to sub-zero temperatures or are cold worked at room temperatures or both, then the structure can transform to a BCC like magnetic structure termed strain induced martensite, resulting from a shear strain at the crystallographic level. This effect, normally counteracted by nickel, was taken into account when deciding the combination of the nickel replacement elements.

45 [0034] Finally, a major drawback of the addition of carbon, nitrogen, manganese or cobalt is the influence these have on the mechanical strength of the steel. Whilst this is desirable from an engineering strength point of view, it is not beneficial in terms of machineability. In metallic materials permanent deformation is accomplished by movement or faulting of tiny imperfections in the crystal lattice of the material (dislocations). The energy required to cause this movement is significantly increased when additions of particularly carbon, nitrogen and manganese are made to the steel. As a result small amounts of deformation cause a large increase in strength. This makes austenitic stainless steels, particularly containing large amounts of C, N, & Mn very difficult to machine as the cutting tool can cause deformation and intense hardening of the steel surface. For this reason the balance of these elements has been carefully controlled so that the machineability of the resulting steel is adequate while the other beneficial properties of the steel discussed above are retained.

50 [0035] The corrosion resistance of the steel according to the invention has been measured several ways with the aim of demonstrating an equivalence to the standard 316-type of chromium, nickel, molybdenum austenitic stainless steel.

[0036] Figure 2 shows the resistance to acid attack on the steel compared with the medical implant grade of 316-type stainless steel and the lower 302-type chromium, nickel austenitic stainless steel. Short samples of wire were exposed to three mineral acids (hydrochloric, sulphuric, and nitric) at a concentration of 1% and a constant temperature of 80°C for periods of up to 42 days. The weight losses were measured and a corrosion rate in grammes/cm²/year calculated. In nitric and sulphuric acids all steels gave similar results but in hydrochloric acid, 316-type had a corrosion rate some 10 times higher whilst 302-type suffered up to almost 100 times more weight loss.

[0037] The superior resistance to chloride attack is demonstrated in Figure 3. In these tests chloride pitting corrosion resistance was assessed by an electrolytic method in which a sample of the steel was immersed in 0.6 molar sodium chloride at room temperature while the potential of the sample relative to a standard reference electrode was slowly increased at a rate of 50 millivolts per minute by polarisation via an inert counter electrode and the current flow recorded. This test demonstrates how easily a steel can protect itself (become passivated) against corrosion. During the test there is a range of voltage where the current flow is minimal and the steel is said to be passive. As the voltage is increased there is a sharp rise in current where pitting corrosion occurs (transpassive range) which, for practical purposes is a current of 50 microamps/cm² or above. The alloy of this invention is shown to give a significantly higher result than the 316-type sample used as a control indicating a very good resistance to chloride pitting attack.

[0038] Further chloride corrosion testing has been conducted in accordance with ASTM B117 which involves exposure to a hot salt spray fog at 35°C and containing 5% sodium chloride. Both 316 stainless steel and this alloy were exposed for a total of 1 month in the exposure chamber. No significant corrosion was observed on either grade of steel.

[0039] Because the alloy is intended to come into contact with the human body its biological toxic effect on cells has been tested. The test conducted was an Agar Overlay Assay cytotoxicity test using L929 cells according to British Standard EN30993-5:1994 and ISO 10993-5:1992. The alloy passed the test and was found to be non-cytotoxic.

[0040] A test involving the wearing of a wrist band made from this alloy is currently ongoing at the time of the filing date of this application, and thus far no corrosion, discolouration or any observable change to the wearers skin has occurred after continuously wearing the band for 6 months previously.

[0041] In terms of the high temperature austenite stability of the alloy, metallurgical examination and simple magnetic tests have shown that even after exposure to annealing temperatures of 1200°C a fully austenitic structure persists with no evidence of the formation of ferrite. Similarly, at cryogenic temperatures down to -196°C, even after cold drawing, no austenite to martensite transformation is observed and the material remains nonmagnetic. Furthermore, during heat treatment of the alloy at normal processing temperatures, no unusual metallurgical changes have been noted that could cause embrittlement such as that produced by the precipitation of chromium carbides (weld decay). When subjected to a standard carbide embrittlement test (Inter Granular Corrosion test to ASTM A262 practice E) all samples have passed.

[0042] In addition to achieving the desired austenite stability, the combination of carbon, nitrogen and manganese contents used in this present invention have had a marked and beneficial effect on improving the mechanical properties of this steel when compared with the well known standard austenitic stainless steels. Table 1 presents the results of mechanical property tests conducted on the alloy in various heat treated and worked conditions at various sizes with for reference purposes results from other austenitic alloys. It is shown that the alloy provides superior strength both in terms of Ultimate Tensile Strength and Yield Strength (0.2% proof stress) whilst maintaining a good level of ductility as measured by elongation. The improved properties are also demonstrated in Figure 4 where the high work hardening rate compared with 302-type stainless steel (traditionally used where high strengths are required) allows the alloy not only to achieve a higher strength but also to achieve similar strength levels with much less deformation, hence retaining more ductility at the given strength level.

[0043] According to the present invention therefore, it is possible to produce a fully stable austenitic stainless steel without the inclusion of nickel in the composition by utilising a metallurgically balanced blend of other austenite stabilising elements, principally manganese, carbon, and nitrogen, whilst allowing the addition of molybdenum so as to improve the corrosion resistance yet whilst at the same time allowing the alloy to be produced in conventional furnaces without the need to for expensive alternative specialised melting equipment.

[0044] In certain circumstances austenite stabilisation may be aided by the addition of cobalt up to a maximum of 10% plus a small copper addition up to 0.9%. As stated above a preferred composition contains carbon 0 to 0.09%, silicon 0 to 0.3%, manganese 14 to 15%, chromium 16 to 18%, molybdenum 2.0 to 2.4%, nitrogen 0.45 to 0.55%, nickel 0.048% maximum, with the remaining percentage being made up of iron. It should be noted that other elements, for example silicon for deoxidation, may be desirable in small quantities and traces of other elements present as impurities may be contained in the new steel without detriment.

[0045] The effects of alloy composition in providing good corrosion resistance and improved mechanical properties when compared with standard austenitic stainless steels are shown in Table 1 and Figures 2, 3 and 4.

Table 1

Mechanical properties of the alloy compared with other steels				
Steel Grade	Condition	UTS N/mm²	0.2% Proof N/mm²	%Elongation
Nickel Free 17-15 CR-Mn (invention)	Billet Forged	1107	913	34.5
	Bar/Rod Annealed	890	473	65
	Wire 43% Cold Reduced	1710	1390	6
Composition D (Medical implant grade) 19-15-3 Cr-Ni-Mo	Billet Forged	671	491	32.5
	Bar/Rod Annealed	567	253	53
	Wire 40% Cold Reduced	1000	840	16
Type 302 18-8 Cr-Ni	Billet Forged	-	-	-
	Bar/Rod/A annealed	680	316	56
	Wire 47% Cold Reduced	1355	1143	4

[0046] In summary therefore, the invention relates to a steel composition which is substantially free of nickel and which can be used for medical implants and/or jewellery manufacture. Some humans experience severe allergic reactions to Nickel and therefore there has been a desire for some time to provide a Nickel free steel. Nickel is an important constituent of surgical grade steel because it is a good austenite promoter, and steel thus formed has good strength properties and has paramagnetic characteristics which are essential for such steels. The absence of Nickel results in the formation of ferritic steel which is ferromagnetic, which cannot be used for medical implants. The invention results from the realisation that Nitrogen is a good promoter of austenitic steel structures, and although Nitrogen is a gas and thus generally insoluble in molten steel, a careful balance of additional alloying elements such as Manganese, Chromium, and Molybdenum, with Iron can result in a molten alloy in which Nitrogen can be dissolved at atmospheric pressure to a degree at which its austenitic steel structure promotion effects are readily appreciable.

Claims

1. An austenitic stainless steel having as essential alloying elements: 0 to 0.15% of carbon, 0 to 0.3% of silicon, 12 to 25% of manganese, 12 to 20% of chromium, 0 to 2.4% of molybdenum, 0.3 to 0.55% of nitrogen, and from 0 to 10% of cobalt, 0 to 0.9% of copper, all percentages being percentages by weight, the remainder being iron together with incidental impurities and a concentration of nickel or less than 0.050%.
2. A steel in accordance with claim 1 wherein the contents of alloying elements are: carbon 0 to 0.09%, silicon 0 to 0.3%, manganese 14 to 15%, chromium 16 to 18%, molybdenum 2.0 to 2.4%, nitrogen 0.45 to 0.55%, and less than 0.048% nickel.
3. A steel in accordance with any preceding claim wherein the composition has 15% of Manganese and 17% of Chromium.
4. A steel in accordance with any preceding claim wherein austenite stabilisation is aided by the addition of Cobalt up to a maximum of 10%.
5. A steel in accordance with any preceding claim wherein the composition further includes Copper up to 0.9% by weight.
6. A steel in accordance with any preceding claim characterised in that the composition is

EP 1 087 029 A2

Carbon 0.09%
Manganese 15%
Chromium 17%
Nitrogen 0.45%
5 Molybdenum 2.2%
 Nickel 0.04%
 Iron 65.22%.

7. A steel as hereinbefore described with reference to the accompanying figures.

10

15

20

25

30

35

40

45

50

55

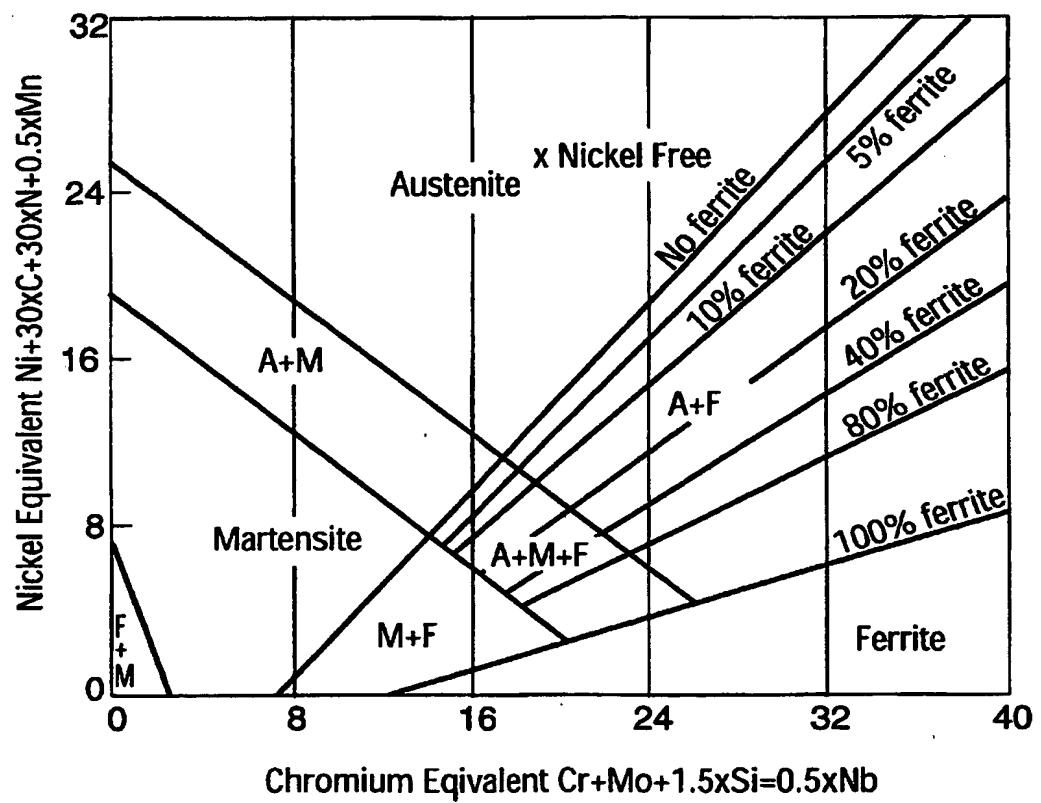


FIG. 1

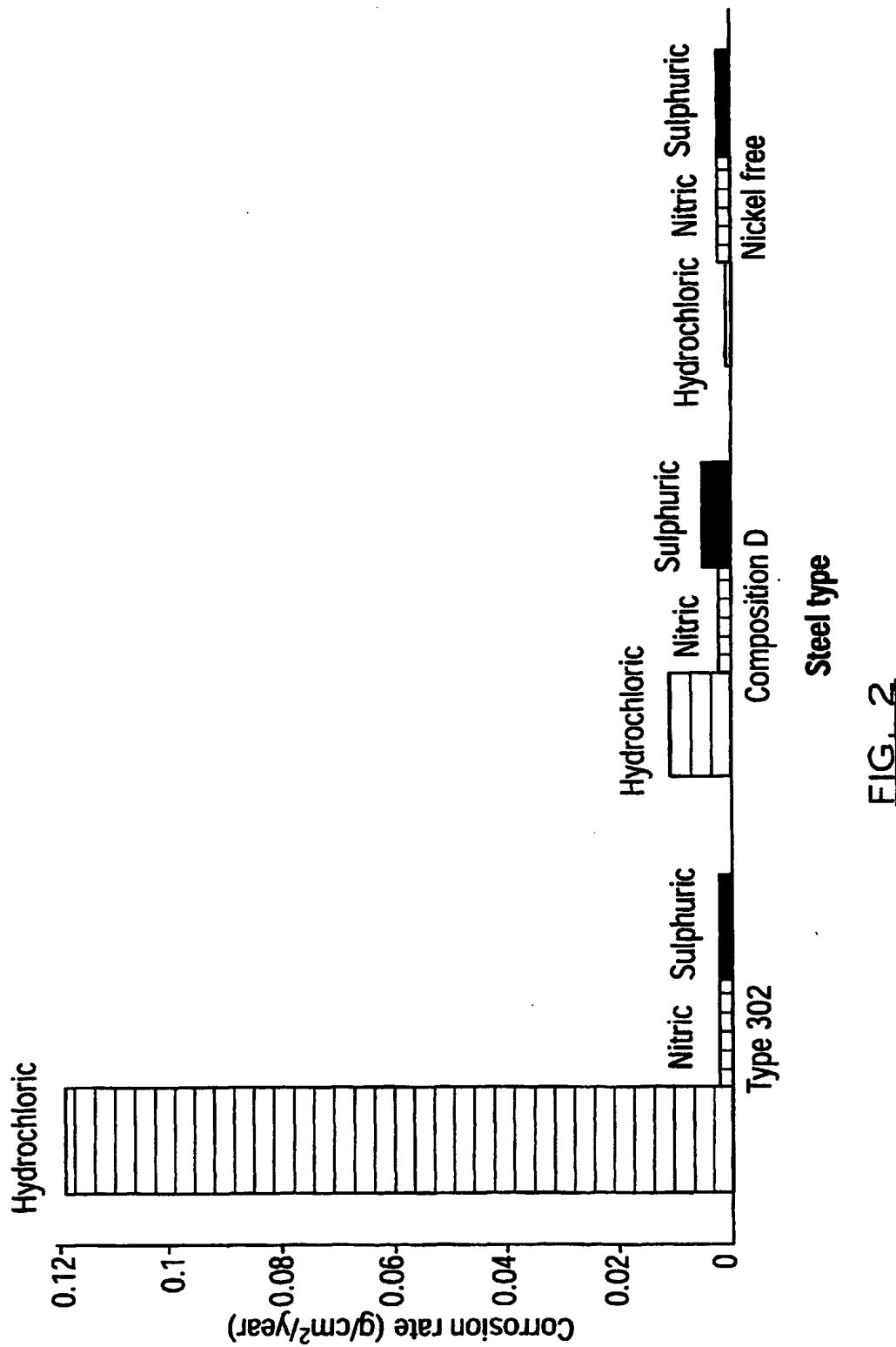


FIG. 2

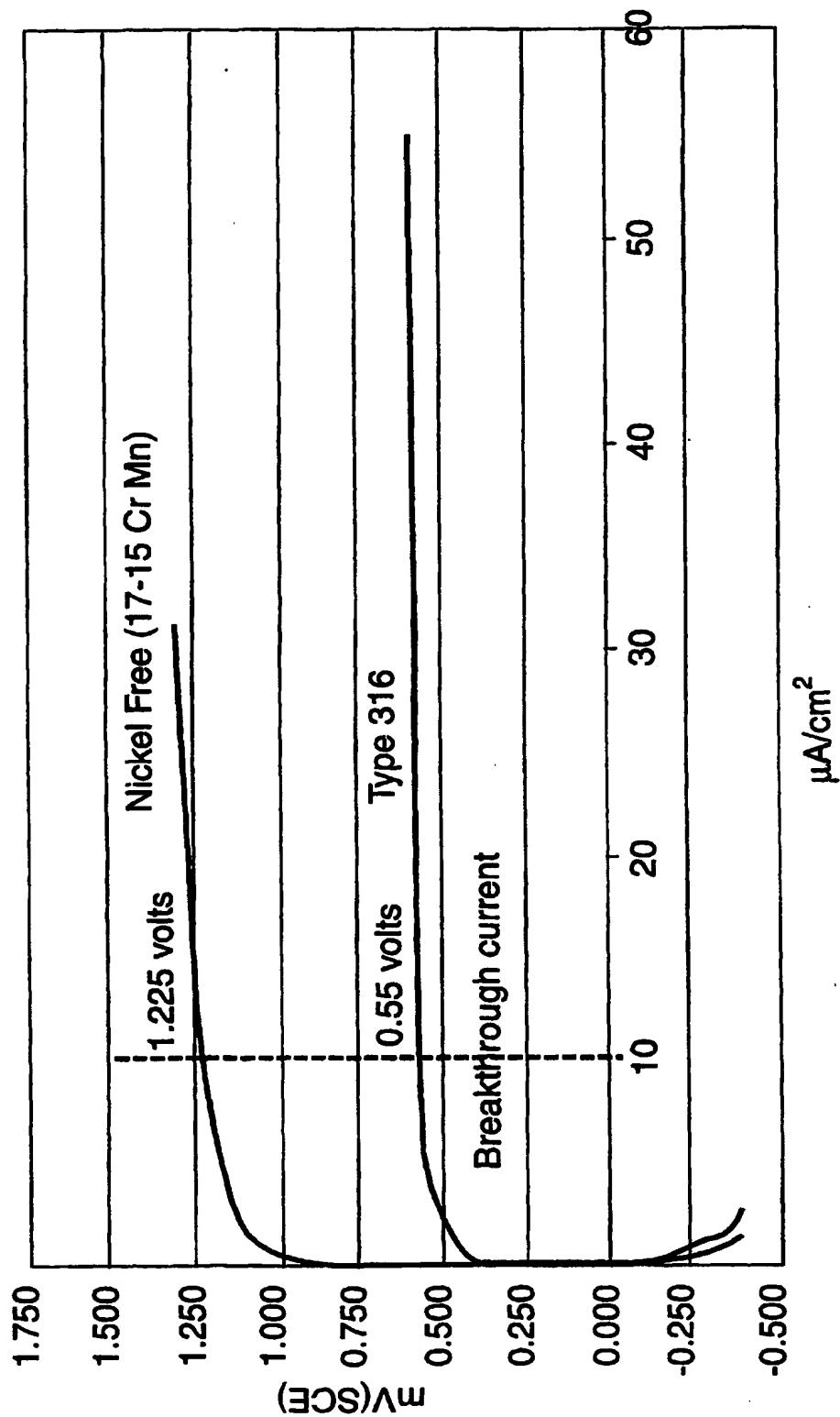


FIG. 3

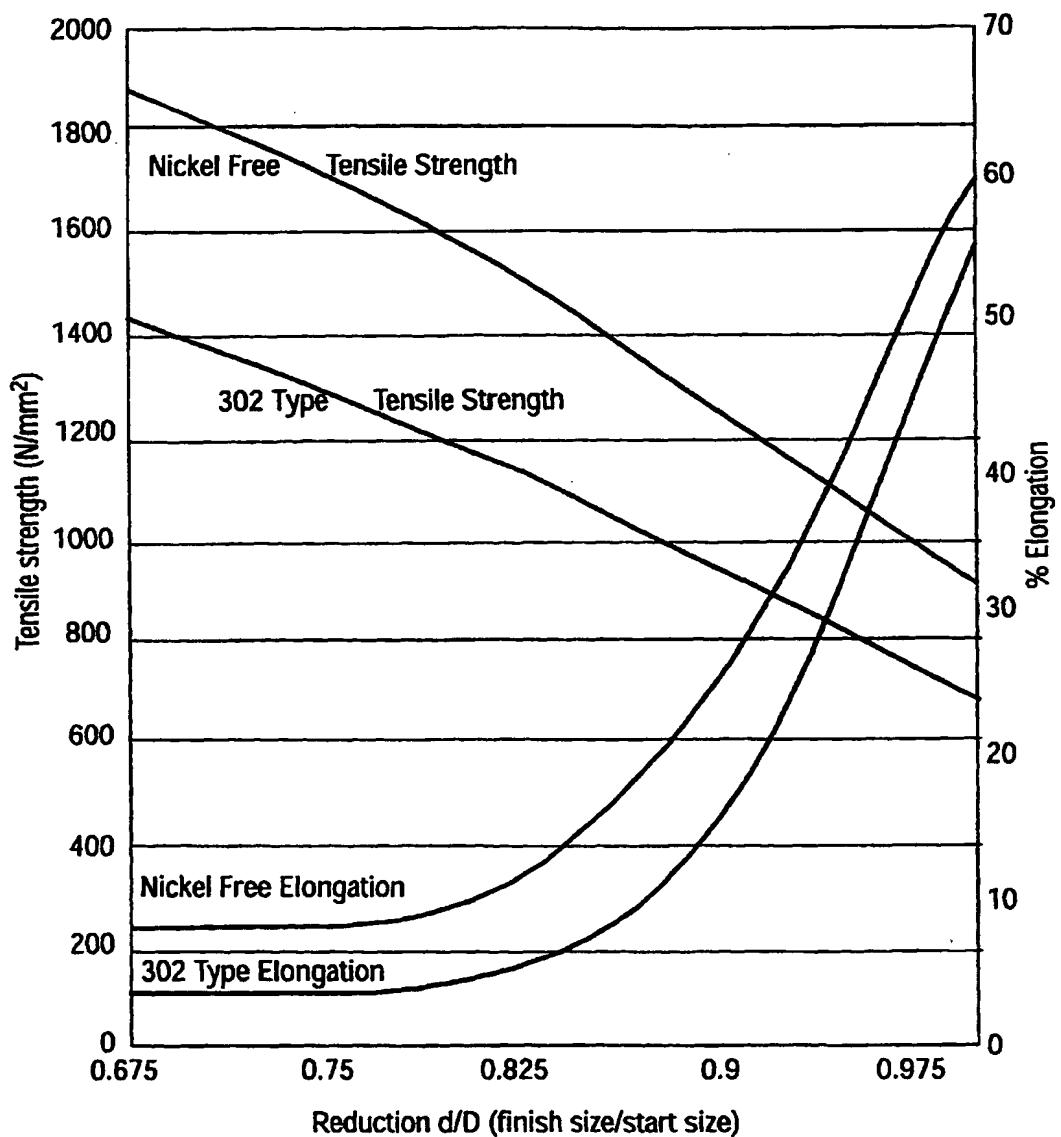


FIG. 4